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DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

1254-0193P

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

10/031635

INTERNATIONAL APPLICATION NO.

PCT/JP00/04893

INTERNATIONAL FILING DATE

July 21, 2000

PRIORITY DATE CLAIMED

July 23, 1999

TITLE OF INVENTION

A RUBBER COMPOSITION FOR EXTRUSION AND MOLDING AND APPLICATIONS THEREOF

APPLICANT(S) FOR DO/EO/US

NAKAHAMA, Hidenari; ISHII, Yuji; HOSOYA, Mikio; KAWASAKI, Masaaki

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39 (1).
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ has been transmitted by the International Bureau. WO 01/07516
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - ✓ a. ☒ is transmitted herewith.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4)
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 20. below concern document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98, Form PTO-1449(s), and International Search Report (PCT/ISA/210) with 0 cited document(s).
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
14. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821-1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information:
 - ✓ 1.) PCT/IB/308
 - ✓ 2.) Four (4) sheets of Formal Drawings

JC13 Rec'd PCT/PTO 23 JAN 2002

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PATENT
1254-0193P

IN THE U.S. PATENT AND TRADEMARK OFFICE

Applicant: NAKAHAMA, Hidenari et al.
Int'l. Appl. No.: PCT/JP00/04893
Appl. No.: New Group:
Filed: January 23, 2002 Examiner:
For: A RUBBER COMPOSITION FOR EXTRUSION
AND MOLDING AND APPLICATIONS
THEREOF

PRELIMINARY AMENDMENT

BOX PATENT APPLICATION

Assistant Commissioner for Patents
Washington, DC 20231

January 23, 2002

Sir:

The following Preliminary Amendments and Remarks are respectfully submitted in connection with the above-identified application.

AMENDMENTS

IN THE SPECIFICATION:

Please amend the specification as follows:

Before line 1, insert --This application is the national phase under 35 U.S.C. § 371 of PCT International Application No. PCT/JP00/04893 which has an International filing date of July 21, 2000, which designated the United States of America.--

Docket No. 1254-0193P

IN THE CLAIMS:

Please amend the claims as follows:

8. (Amended) A weather strip sponge product, highly expanded seal product, glass run channel product, window frame product or water hose product for automobile characterized by comprising the rubber composition according to claim 1.

9. (Amended) A process for manufacturing a vulcanized rubber molding product comprising molding the rubber composition according to claim 1 to an intended shape using an extruder and vulcanizing it.

16. (Amended) The rubber composition for molding according to claim 10, wherein, the composition does not break in a ribbon preformed prior to injection and has a good fluidity in mold which does not vary, and physical properties of the composition after vulcanization do not vary depending on mixing conditions in a preparation of the compound.

17. (Amended) A rubber vibration insulator, cast sponge, grommet, O-ring, packing, boots, window frame, break piston cup or OA roll product characterized by comprising the rubber composition according to claim 10.

Docket No. 1254-0193P

18. (Amended) A process for manufacturing a vulcanized rubber molding product comprising forming the rubber composition according to claim 10 to a shape suitable to a molding machine and then vulcanizing it.

Docket No. 1254-0193P

REMARKS

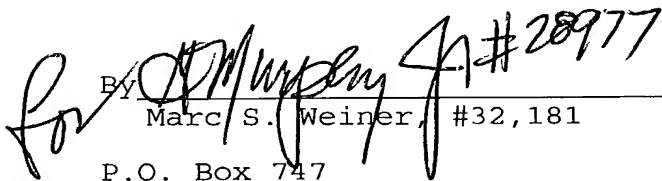
The specification has been amended to provide a cross-reference to the previously filed International Application.

The claims have been amended to delete improper multiple dependencies and to place the application into better form for examination. Entry of the above amendments is earnestly solicited. An early and favorable first action on the merits is earnestly solicited.

If necessary, the Commissioner is hereby authorized in this, concurrent, and future replies, to charge payment or credit any overpayment to Deposit Account No. 02-2448 for any additional fees required under 37 C.F.R. § 1.16 or under 37 C.F.R. § 1.17; particularly, extension of time fees.

Respectfully submitted,

BIRCH, STEWART, KOLASCH & BIRCH, LLP

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MSW/cqc
1254-0193P

Attachment: VERSION WITH MARKINGS TO SHOW CHANGES MADE

Docket No. 1254-0193P

18. (Amended) A process for manufacturing a vulcanized rubber molding product comprising forming the rubber composition according to [any one of claims 10 - 16]claim 10 to a shape suitable to a molding machine and then vulcanizing it.

(Rev. 11/13/01)

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10031635 10/031635
JC13 Rec'd PCT/PTO 23 JAN 2002

DESCRIPTION

A RUBBER COMPOSITION FOR EXTRUSION AND MOLDING AND APPLICATIONS THEREOF

Technical Field

This invention relates to a rubber composition for extrusion and molding and applications thereof.

Background Arts

An ethylene / α -olefin / non-conjugated polyene copolymer rubber such as ethylene / propylene / diene copolymer rubber (EPDM) is widely used for automotive parts, household electric appliance parts, and the like thanks to superior weatherability, heat resistance and ozone resistance.

Among these, materials for sealant or fillers (packing) for automobiles and household electric appliances are the products manufactured by a continuous extrusion molding process.

Requirements for such rubber extrusion composition are continuous feedability to extruder and no occurrence of crack or tear in a ribbon-like compound preformed prior to an extrusion during its storage.

During extrusion process, cross-sectional area of extrudate should not change, that is, die swell ratio should not vary. Variation in die swell ratio leads to change in cross-sectional shape of glassrun or window frame products and may results in lowering of sealing performance and inferior products. Furthermore, in weather strip sponge products, the materials varying in the die swell ratio cause a big problem of uneven foaming

since the variation means uneven viscoelastic state in the material.

In addition to these, in extrudate products of EPDM containing carbon black, trouble of foreign matter coming from unknown cause occurs very often. Analysis of a portion of the foreign matter for its cause survey often results in that the portion is composed of the same components to rubber substrate. Mysteiously this trouble naturally disappears, and occurs again sometimes.

On the other hand, there are many products manufactured by molding process in the rubber molding technology. Rubber vibration isolator obtained by injection is one of the products using a rubber composition for molding. Materials for injection are fed as a ribbon-like compound sheeted out using a roll. Tear of the ribbon lowers stability of material feeding and makes continuous production impossible. Such a material may show an abrupt viscosity increase in a feeder of the injection machine and leads to poor flow in a mold after injection. The products molded in such state often had a trouble such as an occurrence of crack during durability test.

Materials used for molding weather strip corner are required to have stable fluidity of the material. Changes of fluidity in each molding cause a serious problem due to poor adhesion at interface with straight parts of weather strip sponge or inferior appearance at joint area.

Fixing roll for copying machine, one of OA rolls, is a foam product having semiconductivity. It often had variation troubles in foaming and electric resistance due to unknown cause.

O-ring product also had troubles of uneven product shrinkage in each molding by unknown cause. Another problem was lowering

in mechanical strength of product even with good product appearance.

Analysis of substrate for cause survey often resulted in no specific difference in the substrate composition. These phenomena are troublesome and mysterious because they naturally disappear after a while and the same troubles occur again sometimes.

At present, these trouble is considered to be caused by formation of a physical network originated in carbon black / rubber interface produced in the compound during mixing. That is, this network causes the troubles described above in molding a product.

To solve such problems, adding of polysulfide compounds including sulfur or sulfur compounds as radical scavenger has been disclosed in JP-A-H7-138379.

The addition of such sulfur or sulfur compounds at loading level of about 1.0×10^{-2} mole per 100 weight parts of polymer in a mixer, however, causes start of crosslinking by the presence of zinc oxide (ZnO) contained in the compound and leads to a problem of gelation (chemical burning). Loading level of about 1.0×10^{-3} mole, 1/10 of the above loading level, is safe in view of the burning in a mixer, but has little effect to solve the problems mentioned above.

Disclosure of the Invention

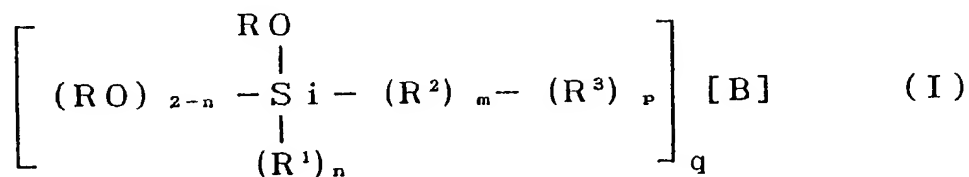
First object of the invention is to solve such problems described above accompanied with conventional technology, and provide a rubber composition for extrusion to give a ribbon-like compound prepared prior to extrusion having no crack nor tear, stable cross sectional shape of extrudate, and foamed products with little variation in foaming, and also products made of the said rubber composition such as weather strip sponge, high

extension seal, glass run channel, window frame and water hose for automobile.

Second object of the invention is to provide a rubber composition for molding to give a compound prepared for injection having no tear phenomenon, superior fluidity in a mold, in addition stable foaming and little variation in foaming in cast sponge, and also products made of the said composition with good surface texture and superior mechanical strength such as rubber vibration isolator, cast sponge, grommet, O-ring, packing, boots, window frame, break piston cup and OA roll products.

The invention includes the following disclosures.

(1) A rubber composition for extrusion comprising 100 weight parts of ethylene / α -olefin / non-conjugated polyene copolymer rubber (A) composed of ethylene, α -olefin having carbon atoms of 3 - 20 and non-conjugated polyene, and at least 30 - 300 weight parts of carbon black (B) and 1.0×10^{-5} - 5.0×10^{-3} mol of alkoxysilane compound (C) shown by the following formula (I):



wherein, R is an alkyl group having carbon atoms of 1 - 4 or an alkoxy group having carbon atoms of 1 - 4, R^1 is an alkyl group having carbon atoms of 1 - 4 or phenyl group, n is 0, 1 or 2, R^2 is a bivalence of linear or branched hydrocarbon group having carbon atoms of 1 - 6, R^3 is an arylene group having carbon atoms of 6 - 12, m and p are 0 or 1 respectively, and m and p are not

0 at a same time, q is 1 or 2, B is -SCN or -SH when q is 1, and -Sx- when q is 2 (wherein x is an integer of 2-8).

(2) The rubber composition for extrusion according to item 1, wherein the ethylene / α -olefin / non-conjugated polyene copolymer rubber (A) (i) comprises a unit (a) derived from ethylene and a unit (b) derived from α -olefin having carbon atoms of 3 - 20 in a [(a) / (b)] molar ratio of 50 / 50 - 90 / 10, (ii) has an iodine value of 1-40, and (iii) has an intrinsic viscosity $[\eta]$ measured in decalin at 135 °C of 2.0 - 4.5 dl/g.

(3) The rubber composition for extrusion according to item 1, wherein an amount of the carbon black (B) is 50 - 200 weight parts to 100 weight parts of the ethylene / α -olefin / non-conjugated polyene copolymer rubber (A).

(4) The rubber composition for extrusion according to item 1, wherein an amount of the carbon black (B) is 61 - 200 weight parts to 100 weight parts of the ethylene / α -olefin / non-conjugated polyene copolymer rubber (A).

(5) The rubber composition for extrusion according to item 1, wherein an amount of the carbon black (B) is 70 - 200 weight parts to 100 weight parts of the ethylene / α -olefin / non-conjugated polyene copolymer rubber (A).

(6) The rubber composition for extrusion according to any one of items 1-5, wherein its apparent activation energy is 20 - 300 kJ/mol, and a change rate of the apparent activation energy is not higher than 40% even after processing in any rubber processing process.

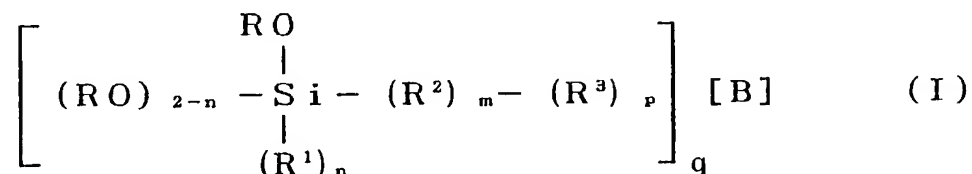
(7) A rubber composition for extrusion, wherein it does not show any ribbon break nor ribbon crack, and has a change rate in die swell ratio not higher than 5% due to a rise of viscosity in an

extruder.

(8). A weather strip sponge product, highly expanded seal product, glass run channel product, window frame product or water hose product for automobile characterized by comprising the rubber composition according to any one of items 1-7.

(9) A process for manufacturing a vulcanized rubber molding product comprising forming the rubber composition according to any one of items 1-7 to an intended shape using an extruder and vulcanizing it.

(10) A rubber composition for molding comprising 100 weight parts of an ethylene / α -olefin / non-conjugated polyene copolymer rubber (A) composed of ethylene, α -olefin having carbon atoms of 3-20 and non-conjugated polyene, and at least 30 - 300 weight parts of carbon black (B) and 1.0×10^{-5} - 5.0×10^{-3} mol of alkoxysilane compound (C) shown by the following formula (I):



wherein, R is an alkyl group having carbon atoms of 1 - 4 or an alkoxy group having carbon atoms of 1 - 4, R^1 is an alkyl group having carbon atoms of 1 - 4 or phenyl group, n is 0, 1 or 2, R^2 is a bivalence of linear or branched hydrocarbon group having carbon atoms of 1 - 6, R^3 is an arylene group having carbon atoms of 6 - 12, m and p are 0 or 1 respectively, and m and p are not 0 at a same time, q is 1 or 2, B is -SCN or -SH when q is 1, and -Sx- when q is 2 (wherein x is an integer of 2-8).

(11) The rubber composition for molding according to item 10, wherein the ethylene / α -olefin / non-conjugated polyene copolymer rubber (A) (i) comprises a unit (a) derived from ethylene and a unit (b) derived from α -olefin having carbon atoms of 3 - 20 in a [(a) / (b)] molar ratio of 50 / 50 - 90 / 10, (ii) has an iodine value of 1-40, and (iii) has an intrinsic viscosity $[\eta]$ measured in decalin at 135 °C of 0.8-4.5 dl/g.

(12) The rubber composition for molding according to item 10, wherein an amount of the carbon black (B) is 50 - 200 weight parts to 100 weight parts of the ethylene / α -olefin / non-conjugated polyene copolymer rubber (A).

(13) The rubber composition for molding according to item 10, wherein an amount of the carbon black (B) is 61-200 weight parts to 100 weight parts of the ethylene / α -olefin / non-conjugated polyene copolymer rubber (A).

(14) The rubber composition for molding according to item 10, wherein an amount of the carbon black (B) is 80 - 200 weight parts to 100 weight parts of the ethylene / α -olefin / non-conjugated polyene copolymer rubber (A).

(15) The rubber composition for molding according to any one of items 10- 14, wherein its apparent activation energy is 20 - 200 kJ/mol, and a change rate change of the apparent activation energy is not higher than 20% even after processing in any rubber processing process.

(16) The rubber composition for molding according to any one of items 10 - 15, wherein, the composition does not break in a ribbon preformed prior to injection and has a good fluidity in mold which does not vary, and physical properties of the composition after vulcanization do not vary depending on mixing conditions in a

preparation of the compound.

(17) A rubber vibration insulator, cast sponge, grommet, O-ring, packing, boots, window frame, break piston cup or OA roll product characterized by comprising the rubber composition according to any one of items 10 - 16. .

(18) A process for manufacturing a vulcanized rubber molding product comprising forming the rubber composition according to any one of items 10 - 16 to a shape suitable to a molding machine then vulcanizing it.

A rubber composition for extrusion and a rubber composition for molding of the invention comprise 100 weight parts of ethylene / α -olefin / non-conjugated polyene copolymer rubber composed of ethylene, α -olefin having carbon atoms of 3 - 20 and non-conjugated polyene (A), and at least 30-300 weight parts of carbon black (B) and $1.0 \times 10^{-5} - 5.0 \times 10^{-3}$ mol of alkoxysilane compound shown by the above described formula (I).

Ethylene / α -olefin / non-conjugated polyene copolymer rubber (A)

α -Olefin having carbon atoms of 3 - 20 in ethylene / α -olefin / non-conjugated polyene copolymer rubber (A) used in the invention specifically includes propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene, 1-eicosene, 9-methyl-1-decene, 11-methyl-1-dodecene, 12-ethyl-1-tetradecene and the like. These α -olefins may be used alone or in combination of two or more. Among these α -olefins, those having carbon atoms of 3 - 8 such as propylene, 1-butene, 4-methyl-1-pentene, 1-hexene and 1-octene are particularly

preferable.

In order to obtain a rubber composition providing vulcanized rubber molded products with superior heat aging resistance, strength characteristics, rubber elasticity, low temperature properties and processability, the ethylene / α -olefin / non-conjugated polyene copolymer rubber (A) preferably comprises (a) an ethylene-derived unit and (b) an α -olefin-derived unit having carbon atoms of 3-20 in [(a) / (b)] molar ratio of 50/50 - 90/10. The [(a) / (b)] molar ratio described above is preferably 65/35 - 90/10, more preferably 65/35 - 85/15 and particularly preferably 65/35 - 80/20.

As a non-conjugated polyene in the ethylene / α -olefin / non-conjugated polyene copolymer rubber (A), a cyclic or linear non-conjugated polyene may be used.

The cyclic non-conjugated polyene includes, for example, dienes such as methyltetrahydroindene, 5-ethylidene-2-norbornene, 5-methylene-2-norbornene, 5-isopropylidene-2-norbornene, 5-vinyl-2-norbornene, 6-chloromethyl-5-isopropenyl-2-norbornene, dicyclopentadiene and norbornadiene; triene such as 2,3-diisopropylidene-5-norbornene, 2-ethylidene-3-isopropylidene-5-norbornene and 2-propenyl-2, 5-norbornadiene.

And as the linear non-conjugated polyene includes, for example, dienes such as 1,4-hexadiene, 3-methyl-1, 4-hexadiene, 4-methyl-1, 4-hexadiene, 5-methyl-1, 4-hexadiene, 4,5-dimethyl-1, 4-hexadiene, 6-methyl-1,6-octadiene, 7-methyl-1,6-octadiene, 6-ethyl-1,6-octadiene, 6-propyl-1,6-octadiene, 6-butyl-1,6-octadiene, 6-methyl-1,6-nonadiene, 7-methyl-1,6-nonadiene, 6-ethyl-1,6-nonadiene, 7-ethyl-1,6-nonadiene, 6-methyl-1,6-decadiene, 7-methyl-1,6-decadiene, 6-methyl-1,6-undecadiene and

7-methyl-1,6-octadiene; and triene such as 4-ethylidene-1,6-octadiene, 4-ethylidene-7-methyl-1,6-octadiene, 4-ethylidene-7-methyl-1,6-nonadiene, 4-ethylidene-6,7-dimethyl-1,6-octadiene, 4-ethylidene-6,7-dimethyl-1,6-nonadiene, 4-ethylidene-1,6-decadiene, 4-ethylidene-7-methyl-1,6-decadiene, 4-ethylidene-7-methyl-6-propyl-1,6-octadiene, 4-ethylidene-1,7-nonadiene, 4-ethylidene-8-methyl-1,7-nonadiene, 4-ethylidene-1,7-undecadiene, 4-ethylidene-8-methyl-1,7-undecadiene, 4-ethylidene-7,8-dimethyl-1,7-nonadiene, 4-ethylidene-7,8-dimethyl-1,7-decadiene, 4-ethylidene-7,8-dimethyl-1,7-undecadiene, 7-ethyl-4-ethylidene-8-methyl-1,7-undecadiene, 4-ethylidene-7,8-diethyl-1,7-decadiene, 4-ethylidene-9-methyl-1,8-decadiene, 4-ethylidene-8,9-dimethyl-1,8-decadiene, 4-ethylidene-10-methyl-1,9-undecadiene, 4-ethylidene-9,10-dimethyl-1,9-undecadiene, 4-ethylidene-11-methyl-1,10-dodecadiene, 4-ethylidene-10,11-dimethyl-1,10-dodecadiene and 3,7-dimethyl-1,4,8-decatriene.

These non-conjugated polyenes may be used alone or in combination of two or more.

In view of obtaining a rubber composition having high crosslinking efficiency and capable to provide vulcanized rubber molded products with superior compression set, along with an advantage in cost, iodine value of the ethylene / α -olefin / non-conjugated polyene copolymer rubber (A) is preferably 1 - 40, more preferably 1 - 30.

In order to obtain a rubber compound to provide vulcanized rubber molded products with superior strength characteristics, compression set and processability, intrinsic viscosity $[\eta]$ of ethylene / α -olefin / non-conjugated polyene copolymer rubber

(A), measured in decalin at 135 °C is preferably 2.0 - 4.5 dl/g, more preferably 2.2 - 4.0 dl/g in the rubber composition for extrusion of the invention, and is preferably 0.8 - 4.5 dl/g, more preferably 0.9 - 4.0 dl/g in the rubber composition for molding.

Carbon black (B)

In the rubber composition for extrusion of the invention, carbon black (B) may be used at 30-300 weight parts, preferably at 50-200 weight parts, more preferably at 61-200 weight parts and most preferably at 70-200 weight parts per 100 weight parts of the ethylene / α -olefin / non-conjugated polyene copolymer rubber (A) in order to obtain a rubber composition to be able to provide vulcanized extruded rubber products with sufficient mechanical strength. And in the rubber composition for molding of the invention, carbon black (B) may be used at 30-300 weight parts, preferably at 50-200 weight parts, more preferably at 61-200 weight parts and most preferably at 80-200 weight parts per 100 weight parts of ethylene / α -olefin / non-conjugated polyene copolymer rubber (A) in order to obtain a rubber composition to be able to provide vulcanized molded rubber products with sufficient mechanical strength.

As the carbon black (B), SRF, GPF, FEF, MAF, HAF, ISAF, SAF, FT, MT and the like may be used. In order to obtain a rubber composition to be able to provide vulcanized rubber molded products with superior mechanical strength and surface texture of products, specific surface area by nitrogen absorption of carbon black (B) is preferably 10-100 m²/g.

Alkoxysilane compound (C)

In the invention, an alkoxysilane compound (C) shown by the formula (I) described above is compounded to reduce a change rate

in activation energy of a compound and suppress the formation of physical network originating from carbon black / polymer interface in the compound during mixing. In order to obtain sufficient effects and maintain vulcanization rate and rubber elasticity, loading level of the alkoxysilane compound (C) should be $1.0 \times 10^{-5} - 5.0 \times 10^{-3}$ mole, preferably $1.0 \times 10^{-4} - 4.0 \times 10^{-3}$ mole and further preferably $1.0 \times 10^{-4} - 2.1 \times 10^{-3}$ mole per 100 weight parts of the ethylene / α -olefin / non-conjugated polyene copolymer rubber (A).

Alkoxysilane compound (C) may be used as an impregnated form into calcium carbonate or carbon black (B) in advance.

In the formula (I) described above, alkyl group having carbon atoms of 1-4 shown as R or R¹ includes, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl and tert-butyl. Alkoxy group having carbon atoms of 1-4 shown as R includes, for example, methoxy, ethoxy, propoxy, isopropoxy, n-butoxy, isobutoxy, sec-butoxy and tert-butoxy. Linear or branched bivalent hydrocarbon group having carbon atoms of 1-6 shown as R² includes, for example, alkylene group such as methylene, dimethylmethylene, ethylene, dimethylethylene, trimethylene, tetramethylene, 1,2-cyclohexylene and 1,4-cyclohexylene; alkylidene group such as cyclohexylidene; arylalkylene group such as diphenylmethylene and diphenylethylene. Arylene group having carbon atoms of 6-12 shown as R³ includes, for example, phenylene, naphthylene and biphenylene.

Typical examples of the alkoxysilane compound (C) shown in the formula (I) described above includes bis-3-(trimethoxysilyl)propyltetrasulfane $[(CH_3O)_3Si-(CH_2)_3-S_4-(CH_2)_3-Si(OCH_3)_3]$, bis-3-(triethoxysilyl)propyltetrasulfane

$[(C_2H_5O)_3Si-(CH_2)_3-S_4-(CH_2)_3-Si(OC_2H_5)_3]$ and bis-3-(tripropoxysilyl)propyltetrasulfane $[(C_3H_7O)_3Si-(CH_2)_3-S_4-(CH_2)_3-Si(OC_3H_7)_3]$.

Other components

A rubber composition for extrusion and molding of the invention may be compounded with additives known in the art other than carbon black (B), such as rubber reinforcing agents, inorganic fillers, softening agents, antioxidants, processing aids, foaming agents, co-foaming agents, vulcanization accelerators, organic peroxides, vulcanization promoters, colorants, dispersing agents, flame retardants and the like, at loading level not impairing purposes of the invention, depending on intended applications of vulcanized products, etc.

The rubber reinforcing agents described above have an enhancing effect on mechanical properties such as tensile strength, tear strength and wear resistance and the like. Typical examples of such rubber reinforcing agents include fine powder of silicic acid, silica and the like. These may be pretreated with silane coupling agents.

Typical examples of silica are fumed silica and precipitated silica and the like. These silica may be applied with surface treatment by reactive silane such as mercaptosilane, aminosilane, hexamethylsilazane, chlorosilane and alkoxylsilane or siloxane of low molecular weight.

Types and loading levels of these rubber reinforcing agents may be suitably selected depending on applications, and maximum loading levels, except for carbon black (B), are generally 150 weight parts, preferably 100 weight parts per 100 weight parts of the ethylene / α -olefin / non-conjugated polyene copolymer

rubber (A).

Typical inorganic fillers described above include light calcium carbonate, ground calcium carbonate, talc, clay and the like.

Types and loading levels of these inorganic fillers may be suitably selected depending on applications and maximum loading levels are generally 300 weight parts, preferably 200 weight parts per 100 weight parts of the ethylene / α -olefin / non-conjugated polyene copolymer rubber (A).

As the softening agents described above, those generally used for rubber may be used. They include, typically, petroleum based softening agents such as process oil, lubricating oil, paraffin oil, liquid paraffin, petroleum asphalt and vaseline; coal tar based softening agents such as coal tar and coal tar pitch; fatty oil based softening agents such as castor oil, linseed oil, rapeseed oil, soybean oil and coconut oil; tall oil; rubber substitute (factice); waxes such as beeswax, carnauba wax and lanolin; fatty acids and salts thereof such as ricinolic acid, palmitic acid, stearic acid, barium stearate, calcium stearate and zinc laurate; naphthenic acid; pine oil, rosin or derivatives thereof; synthetic polymer materials such as terpene resin, petroleum based resin, atactic polypropylene and coumarone-indene resin; ester based softening agents such as dioctyl phthalate, dioctyl adipate and dioctyl sebacate; microcrystalline wax, liquid polybutadiene, modified liquid polybutadiene, liquid Thiokol, hydrocarbon based synthetic lubricating oil and the like. Among these, petroleum based softening agents, in particular, process oil is suitably used. Loading levels of these softening agents may be selected depending on applications of vulcanized products.

The antioxidants described above include, for example, amine based, hindered phenol based or sulfur based antioxidant and the like, and may be used in the range of loading level not to impair purposes of the invention. Amine based antioxidants include diphenylamine, phenylenediamine and the like. Sulfur based antioxidants include those usually adopted in rubber.

As the processing aids described above, those generally adopted in rubber processing may be used. Typically, higher fatty acids such as linoleic acid, ricinolic acid, stearic acids, palmitic acid and lauric acid; salts of higher fatty acids such as barium stearate, zinc stearate and calcium stearate; esters of higher fatty acids described above and the like are included. These processing aids may be used at not more than 10 weight parts, preferably not more than 5 weight parts per 100 weight parts of the ethylene / α -olefin / non-conjugated polyene copolymer rubber (A), however, it is desirable to suitably determine an optimal amount depending on required physical properties.

Foaming agents typically include inorganic foaming agents such as sodium bicarbonate, sodium carbonate, ammonium bicarbonate, ammonium carbonate and ammonium nitrite; nitroso compounds such as N,N'-dimethyl-N,N'-dinitrosoterephthalamide and N,N'-dinitrosopentamethylenetetramine (DPT); azo compounds such as azodicarbonamide (ADCA), azobisisobutyronitrile (AZBN), azobiscyclohexylnitrile, azodiaminobenzene and barium azodicarboxylate; sulfonylhydrazide compounds such as benzenesulfonylhydrazide (BSH), toluenesulfonylhydrazide (TSH), p,p'-oxybis(benzenesulfonylhydrazide) (OBSH) and diphenylsulfone-3,3'-disulfonylhydrazide; azide compounds such as calcium azide, 4,4'-diphenyldisulfonylazide and p-

toluenesulfonylazide.

These foaming agents may generally be used at the ratio of 0.5 - 30 weight parts, preferably 1 - 20 weight parts per 100 weight parts of the ethylene / α -olefin / non-conjugated polyene copolymer rubber (A). Use of the foaming agents at the ratio described above enables manufacturing of a foamed product with apparent specific gravity of 0.03 - 0.8 g/cm³ for the rubber composition for extrusion of the invention, and a foamed product with apparent specific gravity of 0.1 - 0.8 g/cm³ for the rubber composition for molding of the invention. However, it is desirable to determine suitably an optimal amount depending on required physical properties.

Co-foaming agents may be used in combination with the foaming agents, if necessary. The co-foaming agents act to lower decomposition temperature, accelerate decomposition of the foaming agents and achieve even foaming. Such co-foaming agents include, for example, organic acids such as salicylic acid, phthalic acid, stearic acid and oxalic acid, urea and derivatives thereof. These co-foaming agents may generally be used at the ratio of 0.01 - 10 weight parts, preferably 0.1 - 5 weight parts per 100 weight parts of the ethylene / α -olefin / non-conjugated polyene copolymer rubber (A), however, it is desirable to determine suitably an optimal amount depending on required properties.

In addition, another rubber known in the arts may be used by blending with the crosslinkable rubber composition of the invention, so long as not to impair objectives of the invention. Such another rubber includes natural rubber (NR), isoprene based rubber such as polyisoprene rubber (IR) and conjugated diene based

rubber such as polybutadiene rubber (BR), styrene-butadiene rubber (SBR), acrylonitrile-butadiene rubber (NBR) and chloroprene rubber (CR).

Vulcanization agents used for vulcanization include sulfur and sulfur compounds. Typical sulfur includes, powder sulfur, precipitated sulfur, colloidal sulfur, surface treated sulfur, insoluble sulfur and the like. Typical sulfur compounds include sulfur chloride, sulfur dichloride, polymeric polysulfide and sulfur compounds to vulcanize a composition by generating active sulfur at vulcanization temperature such as morpholine disulfide, alkylphenol disulfide, tetramethylthiuram disulfide, dipentamethylenethiuram tetrasulfide, Selenium dimethyldithiocarbamate and the like. Sulfur is preferable among these. Sulfur and sulfur compounds may generally be used at the ratio of 0.1-10 weight parts, preferably 0.5-5 weight parts per 100 weight parts of the copolymer rubber (A) described above.

In using sulfur or sulfur compounds as vulcanization agents, combined use of vulcanization accelerators is preferable. Typical vulcanization accelerators include sulfenamide compounds such as N-cyclohexyl-2-benzothiazolesulfenamide (CBS), N-oxydiethylene glycol-2-benzothiazolesulfenamide (OBS), N-t-butyl-2-benzothiazolesulfenamide (BBS) and N,N -diisopropyl-2-benzothiazolesulfenamide; thiazole compounds such as 2-mercaptobenzothiazole (MBT), 2-(2,4-dinitrophenyl)mercaptobenzothiazole, 2-(4-morpholinodithio)benzothiazole, 2-(2,6-diethyl-4-morpholinothio)benzothiazole and dibenzothiazyl disulfide; guanidine compounds such as diphenylguanidine (DPG), triphenylguanidine, diorthotolylguanidine (DOTG),

orthotolylbiguanide and diphenylguanidine phthalate; aldehyde amine or aldehyde-ammonium type compounds such as acetaldehyde-aniline condensed compounds, butylaldehyde-aniline condensed compounds, hexamethylenetetramine (H) and acetaldehyde ammonia; imidazoline compounds such as 2-mercaptoimidazoline; thiourea compounds such as thiocarbanilide, diethylthiourea (EUR), dibutylthiourea, trimethylthiourea and diorthotolylthiourea; thiuram compounds such as tetramethylthiuram monosulfide (TMTM), tetramethylthiuram disulfide (TMTD), tetraethylthiuram monosulfide, tetrabutylthiuram disulfide, tetrakis(2-ethylhexyl)thiuram disulfide (TOT) and dipentamethylenetetraethiuram sulfide (TRA); salts of dithiocarbamic acid such as zinc dimethyldithiocarbamate, zinc diethyldithiocarbamate, zinc di-n-butylthiocarbamate, zinc ethylphenyldithiocarbamate, zinc butylphenyldithiocarbamate, sodium dimethyldithiocarbamate, Selenium dimethyldithiocarbamate and tellurium dimethyldithiocarbamate; xanthate such as zinc dibutylxanthate; compounds such as zinc white (zinc oxide); and the like. These vulcanization accelerators may generally be used at the ratio of 0.1-20 weight parts, preferably 0.2-10 weight parts per 100 weight parts of the copolymer rubber (A) described above.

Preparation of a rubber composition and vulcanized rubber molded body thereof

The rubber composition of the invention may be prepared by mixing ethylene / α -olefin / non-conjugated polyene copolymer rubber (A), carbon black (B), alkoxysilane compound (C) and additives such as rubber reinforcing agents, inorganic fillers and softening agents using an internal mixer (closed type mixer)

such as Bumbury's mixer and kneader at 80 - 170 °C for 2 - 20 min., followed by additional mixing of sulfur together with optional vulcanization accelerators, vulcanization aids, foaming agents and co-foaming agents using a roll such as open role or kneader at roll temperature of 40 - 80 °C for 5 - 30 min., then sheeting out.

The rubber composition for extrusion of the invention prepared as described above may be shaped as intended by an extruder and vulcanized at 140 - 270 °C for 1 - 30 min. simultaneously with the extrusion or by introducing the extrudate into a vulcanization chamber. Vulcanization process is generally carried out continuously. As a heating method in the vulcanization chamber, a heating measure such as hot air, fluidized bed of glass beads, molten salt bath (LCM), PCM (Powder Curing Medium or Powder Curing Method), UHF (ultra high frequency microwave), steam and the like may be used.

And the rubber composition for molding of the invention prepared as described above may be shaped suitably for a molding machine for molded products. Sheet-like compound is prepared using a roll, etc in advance for a compression molding and vulcanization machine. In an injection, ribbon-like compound is sheeted out from a roll and stored until molding. In a transfer molding of cast sponge products, boll-like compound is prepared in advance. The compounds thus prepared may be vulcanized by heating at 140 - 270 °C for 1 - 30 min.

The inventors, after thorough investigation on the problems accompanied with conventional technology, clarified that the cause is changes in compound viscosity depending on mixing conditions in the ethylene / α -olefin / non-conjugated polyene

copolymer rubber system loaded with carbon black. The inventors presumed that the cause is formation of a network between interfaces of carbon black / polymer (Fig.1) since this phenomenon is specified to the compound system loaded with carbon black. The larger the specific surface area of carbon black is and the higher the loading level of carbon black is, the easier this network tends to be formed. The network also tends to be formed at higher mixing temperature when mixing time is longer. Formation of such network or use of material with generation of origins of such network at carbon black / polymer interfaces results in an abrupt increase in viscosity in an extruder or a mold. It then impairs the production of extrudate due to change in cross sectional shape, that is, change in die swell ratio in the composition for extrusion, and causes fluctuation of fluidity, change in product shrinkage or poor foaming in the composition for molding. Furthermore, in any case of the rubber composition for extrusion and molding, a ribbon crack phenomenon occurs, that is, cracks occur at bending part of the compound during storage after mixing in a mixer and forming to a ribbon-like compound, and thus leads to a serious problem like a lowering in continuous productivity.

For a rubber composition for extrusion and molding, it is very important not to have such viscosity increase which is closely relating to inferior product ratio.

For a further precise explanation, this network means structural change occurred inside a compound.

As an index to express the structural change in the compound by mixing, an apparent activation energy is used in the Examples described hereinafter. The activation energy is obtained from a temperature dependency of viscosity, and determined by quality

of the polymer to be used, compounding of carbon black and the like and loading levels of these materials. Its value becomes smaller when the network (physical structural change) described above is formed.

The inventors, after a thorough investigation, found that the apparent activation energy of the rubber composition for extrusion should be 20 - 300 kJ/mole, preferably 30 - 250 kJ/mole, and more preferably 30 - 200 kJ/mole, and also that a change rate between the apparent activation energy after mixing by rubber mixer and that of right after extrusion in the next process should be not higher than 40 %, preferably not higher than 30 %, and more preferably not higher than 25 % to solve the problems associated with conventional technology. Similarly, the inventors found that the apparent activation energy of the rubber composition for molding should be 20 - 200 kJ/mole, preferably 30 - 150 kJ/mole, and more preferably 30 - 120 kJ/mole, and also that a change rate between the apparent activation energy after mixing by rubber and that of sheet-like, ribbon-like or ball-like compound in the case of transfer molding should be not higher than 20 %, preferably not higher than 15 %, and further preferably not higher than 10 % to solve the problems associated with conventional technology.

Here, the apparent activation energy can not be measured in the presence of vulcanization agents because vulcanization proceeds during the measurement. Therefore, it was evaluated using the compounds without the vulcanization agents in the Examples described hereinafter. In ordinary production, ribbon-like compounds, materials extruded from extruder or compounds before molding contain the vulcanization agents. Results obtained by measurement of the apparent activation energy to grasp and control

the effects of the invention do not change by the presence or absence of the vulcanization agents.

Based on these consideration, in preparation of the rubber composition for extrusion of the invention, it is desirable to mix under such conditions that the apparent activation energy of compound (1) obtained by the mixing procedure according to JIS K6395 with an open roll of 8 inch ϕ becomes generally 20 - 300 kJ/mole, preferably 30 - 250 kJ/mole, and further preferably 30 -200 kJ/mole. Furthermore, it is desirable to mix under such conditions that the apparent activation energy of compound (2) obtained by mixing with a mixer usually used in the rubber industry and then extruding with a extruder for rubber becomes 20 - 300 kJ/mole and the change rate (%) of the activation energy expressed by the following formula:

$$[1 - (\text{apparent activation energy of compound (2)}) / (\text{apparent activation energy of compound (1)})] \times 100$$

becomes generally not higher than 40 %, preferably not higher than 30 %, and more preferably not higher than 20 % as the result of the reaction between carbon black (B) and alkoxysilane compound (C) (silane coupling agent).

And also, in preparation of the rubber composition for molding of the invention, it is desirable to mix under such conditions that the apparent activation energy of compound (1) obtained by the mixing procedure according to JIS K6395 with an open roll of 8 inch ϕ becomes generally 20 - 200 kJ/mole, preferably 30 - 150 kJ/mole, and further preferably 30 - 120 kJ/mole. Furthermore, it is desirable to mix under such conditions that the apparent activation energy of compound (2) obtained by mixing with a mixer usually used in the rubber industry and then forming to sheet-like

for molding or ribbon-like for injection becomes 20 - 200 kJ/mole and the change rate (%) of the activation energy expressed by the following formula:

$$[1 - (\text{apparent activation energy of compound (2)} / (\text{apparent activation energy of compound (1)}))] \times 100$$

becomes generally not higher than 20 %, preferably not higher than 15 %, and more preferably not higher than 10 % as a result of the reaction between carbon black (B) and alkoxysilane compound (C) (silane coupling agent).

Under coexistence of zinc oxide and silane coupling agent, the silane coupling agent react with zinc oxide first resulting in decrease of the silane coupling agent to be combined with carbon black surface, increased change rate of the activation energy of the material, and lowering of the effect of the silane coupling agent. That is, the change rate of the activation energy of material becomes an important parameter to obtain the effect of the silane coupling agent.

In the Examples described hereinbelow, reasons for adopting the activation energy of compounds mixed with an open roll of 8 inch ϕ as the standard are: No formation of the network described above in a compound due to low mixing temperature (temperatures of front roll / back roll = 50 °C / 50 °C), and expectable stabilization of radicals generated by polymer chain scission induced by shear due to presence of oxygen, along with possible better dispersion of carbon black, etc. compared with other mixers. The network among carbon black / polymer interfaces discussed in the invention is hardly formed in an open state (in the presence of oxygen) and at mild mixing temperature. In order to quantify and control amount of the network formed in a closed type mixer

generally used in mixing process in the rubber industry, the state of network is quantified using the apparent activation energy as a standard value. Larger change rate in apparent activation energy by mixing means more network formation in a mixer and gives the problems of ribbon crack or tear. Furthermore, even if such phenomena do not happen in a mixer, the compound with origin of network formation gives abrupt increase in viscosity and thus resulting in fluctuation of fluidity or extrusion output, changes in product cross sectional shape or shrinkage and inferior foaming.

Reasons for the suppression effect of alkoxysilane (C) on network formation is rapid reaction of silanol functional group in its chemical structure with active species (carboxyl group, lactone, hydroxyl group, ketone group and phenol group) at carbon black surface and rapidly covering the surface during reaction, along with stabilization effect of polysulfide group on the origin points (at carbon black / polymer interface) for network formation among the interfaces.

That is, alkoxysilane (C), even in very small amount, effectively and rapidly disperses to carbon black / polymer interfaces, cause points for viscosity increase to raise the problem in extrusion and molding of a compound material, and stabilizes origin sites of network formation and thus suppresses the network formation. Since this effect is obtained with very small amount there is no fear of burning in mixing, a problem of polysulfide compounds such as sulfur in conventional technology described above.

A vulcanized rubber product thus obtained are used for sponge weather strip, seal products with high extension, glassrun channel,

window frame and water hose for automobile, in the rubber composition for extrusion of the invention, whereas rubber vibration isolator, cast sponge, grommet, O-ring, packing, boots, window frame, break piston cup and OA roll, in the rubber composition for molding of the invention.

Brief Description of the Drawings

Fig. 1 shows a state of physical network formation among carbon black / polymer interfaces

Fig. 2 shows measurement method for shape retention ratio, wherein a and b designate vertical and horizontal direction, respectively.

Fig. 3A shows a top view of a molded product used for the fluidity test in Examples and Fig. 3B shows its cross sectional view.

Fig. 4A shows a front view of tubular sponge manufactured in Examples and Fig. 4B shows its cross sectional view.

In Figs. 3 and 4, 1 shows tubular sponge, and in Fig. 3, 2 shows a molded product.

This specification includes part or all of contents as disclosed in the specifications of Japanese Patent Applications Nos. 11(1999)-209036 and 11(1999)-223639, which are the base of the priority claim of the present application.

Best Mode for Carrying out the Invention

The invention will be further explained specifically by Examples and Comparative Examples that follow, however, the scope of the invention should not be restricted by these Examples.

Various physical properties and their measurement methods in

Examples and Comparative Examples are as follows.

[Apparent activation energy]

1) Measurement was carried out using RDS-II made by Rheometric Co., Ltd.

2) Sample preparation: A sheets of 2 mm thickness was prepared from a compound containing no vulcanization agent nor accelerator at 190 °C for 5 min. using 50 ton press machine.

3) Measurement conditions: Complex viscosity coefficient was measured at each temperature of 170 °C, 190 °C and 210 °C under frequency of 0.1 - 15 Hz (strain: 1 %, stabilization time at each temperature: 3 min.).

4) Calculation of activation energy

Frequency dependencies of complex viscosity coefficient were measured at 170 °C, 190 °C and 210 °C, and apparent activation energy at 190 °C was obtained according to the following equations.

$$a_T = A \exp [E_a / R (T - T_{ref})]$$

$$\eta_T = a_T \eta_{T0}$$

η_T and η_{T0} : Complex viscosity coefficient at T and T_0 , respectively, T_{ref} : Standard temperature (190 °C),

a_T : Shift factor,

A: Frequency factor,

E_a : Apparent activation energy,

R: Gas constant

T: Temperature.

Quantification index of network (physical structural change):

(For rubber composition for extrusion)

$$\text{Change rate of activation energy (\%)} = [1 - ((2) / (1))] \times 100$$

(1) : Standard value = Apparent activation energy of a compound obtained by mixing on an open roll of 8 inch ϕ for 21 min.

(2) : Apparent activation energy of a compound right after injection by an injection machine in the next process.

(For rubber composition for molding)

Change rate of activation energy (%) = $[1 - ((2) / (1))] \times 100$

(1) : Standard value = Apparent activation energy of a compound obtained by mixing on an open roll of 8 inch ϕ in accordance with JIS K6395.

(2) : Apparent activation energy of a sheet-like compound prepared for molding or a ribbon-like compound prepared for injection in the next process.

[Die swell ratio]

A compound containing no vulcanization agent nor accelerator was wound on an open roll of 8 inch ϕ (roll clearance: 5 mm) and mixed for 2 min. then sheeted out in ribbon-like shape. The compound was then fed to 50 mm extruder SCER (made by Shimadzu Corp.) and extruded through a nozzle with $L/D = 60 \text{ mm} / 2 \text{ mm}$ under shear rate of 10^2 sec^{-1} and diameter of cross section (A) (mm) of extrudate was measured. Die swell ratio was obtained according to the following formula.

die swell ratio = $A / 2$ (nozzle diameter in mm)

[Ribbon crack test] (For rubber composition for extrusion)

A ribbon-like compound was cut to 30 cm in length, folded at the center and both ends were fixed. Bending surface was checked on crack and breakage after leaving in an oven at 40°C for 24 hrs.

[Ribbon tear and breakage test] (For rubber composition for molding)

A ribbon-like compound with the dimension of 5 mm T \times 40 mm W \times 300 mm L was prepared using a roll of 8 inch ϕ and stored in an oven at 40°C for 1 hr. The ribbon was then extended to 350 mm and

occurrence of tear and breakage was evaluated.

[Próduct surface texture (sensory inspection)]

A tubular sponge rubber was cut to 30 mm in length, irradiated from above with 60 W lamps, and checked visually from the angle at which surface looked glossy (full mark is 5 point).

5 point: strongly glossy with smooth surface

3 point: glossy but with relatively rough surface

1 point: no gloss with rough surface

(4 or 2 point means intermediate level between 5 and 3 points and 3 and 1 points respectively)

[Mooney viscosity]

Mooney viscosity (V_m) was obtained at 140 °C on green rubber according to JIS K6300, and Mooney scorch time (t_5) was determined at 125 °C.

[M_{100} (100 % Modulus)]

It was measured in accordance with JIS K6251.

[M_{300} (300 % Modulus)]

It was measured in accordance with JIS K6251.

[Tensile test] (For rubber composition for extrusion)

A vulcanized rubber sheet was obtained at 170 °C for 10 min. using a 150 ton press machine. Tensile strength at break (T_b) and elongation at break (E_b) were measured at 23 °C under 500 mm / min of rate of tension in accordance with JIS K6251.

[H_A (Product Hardness)] (For rubber composition for extrusion)

Product hardness was measured with vulcanized sheet of 2 mm thick piled up to 12 mm using durometer A in accordance with JIS K6253.

[Tensile test and Hardness test] (For rubber composition for molding)

A vulcanized rubber sheet was obtained at 170 °C for 10 min. using

a 150 ton press machine. Tensile strength at break (T_b), elongation at break (E_b) and hardness (H_A) were measured at 23 °C under 500 mm / min of rate of tension in accordance with JIS K6251.

[Compression set test]

(1) Rubber composition for automobile glassrun channel and window frame and products thereof

Test pieces vulcanized at 170 °C for 15 min were used under the test conditions of 70 °C × 22 hrs in accordance with JIS K6262 (1993).

(2) Weatherstrip sponge products

A tubular sponge rubber vulcanized in hot air and cut to a length of 30 mm was compressed to a half of the height before loading, and held in a gear oven together with a fixture at 70 °C for 200 hrs. Height of the test piece was measured after taking out of a compression fixture then cooling for 30 min. Compression set was calculated according to the following formula.

$$\text{Compression set} = [(t_0 - t_1) / (t_0 - t_2)] \times 100 (\%)$$

t_0 : Height of sample before test

t_1 : Height of sample after thermal treatment and cooling for 30 min.

t_2 : Height of sample in the state fixed to a fixture

(3) Rubber composition for molding

Compression set was measured with the test piece vulcanized at 170 °C for 12 min. under the test conditions of 120 °C × 22 hrs. in accordance with JIS K6262 (1993).

[Dynamic viscoelasticity test]

Dynamic viscoelasticity test was carried out using RSA-2 tester (made by Scientific Far East Co., Ltd.) at 25 °C, frequency of 1 Hz / 100 Hz and strain ratio of 0.1 % to obtain complex modulus

of elasticity E^* ($\times 10^7$ dyne/cm²). In addition, dynamic-to-static modulus ratio (index for noisiness in a car) and loss tangent ($\tan \delta$) (index for driving comfortableness) were obtained by the formulas below.

$$E^* = E' + iE''$$

(E^* : Complex modulus of elasticity, E' : Dynamic modulus of elasticity, E'' : Dynamic loss modulus of elasticity)

$$\text{Dynamic-to-static modulus ratio} = E^* \text{ at } 100 \text{ Hz} / E^* \text{ at } 1 \text{ Hz}$$

$$\tan \delta = E'' / E'$$

[Foreign matter test for extrusion products]

A flat plate was prepared from a ribbon-like compound by extruding using 60 mm thick extruder and vulcanizing in a microwave vulcanization chamber (UHF, 200 °C, 3 kW) and a hot air vulcanization chamber (HAV, 230 °C) connected in series at take-up speed of 7 m/min. Number of foreign matter (not smaller than 0.03 mm) on surface per 1 m was counted.

[M25 (25 % Tensile stress)]

(a) Test piece: Punched with JIS NO.1 dumb-bell.

(b) Measurement method: Stress at 25 % strain was measured at the rate of extension of 50 mm/min.

[Specific gravity]

A test piece of 20 mm \times 20 mm was punched out from hot air vulcanized tubular sponge rubber. Dust on surface was wiped off with alcohol. Masses of this test piece in air and pure water were measured using an automatic specific gravimeter (made by Toyo Seiki Seisaku-Syo Ltd., model M-1) at 25 °C. Specific gravity SG of sponge was calculated from difference of both masses.

[Water absorption ratio (Wa)]

A test piece of 20 mm \times 20 mm was punched out from hot air

vulcanized tubular sponge rubber. Dust on surface was wiped off with alcohol. The test piece was immersed in water at depth of 50 mm and held for 3 min under 125 mmHg. Then, after leaving the test piece for 3 min. under atmospheric pressure, weight of the test piece with water absorbed was measured, and water absorption ratio (Wa) was calculated according to the following formula.

$$W_a \text{ (weight \%)} = [(w_2 - w_1) / w_1] \times 100$$

W_1 : Weight before immersion (g)

W_2 : Weight after immersion (g)

[Shape retention ratio (%)]

A test piece having length of 2 mm was cut out from hot air vulcanized tubular sponge rubber. Shape retention ratio (%) was calculated according to the following formula by measuring vertical and horizontal dimensions, a and b, using magnifying glass (see Fig. 2).

$$\text{Shape retention ratio (\%)} = [(a - b) / a] \times 100$$

[Fluidity test]

Rubber compound (10 g) was charged into a transfer mold in 10 sec. and vulcanized and foamed at the mold temperature of 180 °C for 3.5 min. Thus obtained vulcanized and foamed rubber molded body shown in Fig. 3 was taken out from mold, and length (L in Fig. 3) of the molded body was measured.

Examples 1-5 and Comparative Examples 1-5 Rubber composition for automobile glassrun channel and window frame and products thereof

A composition including the following components was mixed using 16 L Bumbury's mixer (made by Kobe Steel, Ltd.) under charge ratio of 75 %: 100 weight parts (110 weight parts as product weight)

of ethylene / propylene / 5-vinyl-2-norbornene copolymer rubber (A-1) [molar ratio of ethylene / propylene = 68 / 32, intrinsic viscosity $[\eta]$ in decalin at 135 °C = 3.0 dl/g, iodine value = 12, Mooney viscosity (after oil extension) = 110, oil content = 10 phr (parts per hundred rubber); product of Mitsui Chem. Corp.] , 175 weight parts of FEF carbon black [Asahi Carbon K.K., trade name: Asahi #60G] , 20 weight parts of ground calcium carbonate [Shiraishi Calcium Kaisha Ltd., trade name: Whiton SB] , 85 weight parts of softening agent [Idemitsu Kosan Co., Ltd., trade name: Diana Process Oil PW-380] , 5 weight parts of zinc white [Sakai Chem. Ind. Co., Ltd., trade name: No. 1] , 1 weight part of stearic acid and dimethyldistearylammonium chloride [Lion Akzo Co., Ltd., trade name: Arquad 2HT-F] .

Mixing procedures were as follows: Firstly, ethylene / propylene / 5-vinyl-2-norbornene copolymer rubber (A-1) was masticated for 15 sec, followed by addition of zinc white, stearic acid, ground calcium carbonate, softening agent and dimethyldistearyl ammonium chloride, and finally carbon black roughly mixed with 0.5 weight parts (1.0×10^{-3} mole) of bis-3-(triethoxysilyl)propyltetrasulfane [Degussa Huels AG., trade name: Si-69] (in Comparative Examples 1 -5, carbon black itself without blending bis-3-(triethoxysilyl)propyltetrasulfane) was charged and mixed for 4 min. after temperature of the mixture reached at 150 °C, with floating weight being maintained in down position. Temperatures of discharged compounds after mixing for 4 min. were as shown in Tables 2 and 3.

The compound thus prepared was then wound around 8 inch ϕ an open roll of 8 mm ϕ (surface temperatures of front and back rolls; 50 °C, rotation speeds of front and back roll; 18 rpm and 15 rpm,

respectively, roll clearance; 5 mm), and then added with sulfur, vulcanization accelerator and calcium oxide [Inoue Sekkai Kogyo K.K., trade name: Vesta #BS] mixed for 5 min. A ribbon-like compound with 10 mm thickness and 70 mm width was sheeted out and fed to a 50 mm extruder for rubber to produce glassrun channel products.

Samples for measurement of activation energy and die swell were prepared similarly by the process described above except for excluding vulcanization agent and vulcanization accelerators in roll mixing.

Formulation of each composition is shown in Table 1 and mixing conditions and results are shown in Tables 2 and 3.

Table 1

	Example	Comparative Example
	1 - 5	1 - 5
(Composition)		
Copolymer Rubber (A-1)	110	110
Zinc Oxide No.1	5	5
Stearic Acid	1	1
Asahi #60G	175	175
Whiton SB	20	20
PW-380	85	85
Si-69	0.5	0
Sanceler 22	0.7	0.7
Sanceler BZ	1.3	1.3
Sanceler MDB	1.3	1.3
Arquad 2HT-F	1.0	1.0
Sulfur	1.0	1.0
Vesta #BS	5	5

Vulcanization system: Sulfur 1.0 weight part, vulcanization

accelerator 2-mercaptoimidazoline [Sanshin Chem. Ind. Co., Ltd., trade name: Sanceler 22] 0.7 weight part, vulcanization accelerator zinc di-n-butyldithiocarbamate [Sanshin Chem. Ind. Co., Ltd., trade name: Sanceler BZ] 1.3 weight part and vulcanization accelerator 2-(4-morpholinodithio)benzothiazole [Sanshin Chem. Ind. Co., Ltd. trade name: Sanceler MDB] 1.3 weight part.

Table 2

	Example				
	1	2	3	4	5
(Mixing Conditions)					
Discharge Temp. - Mixing Time					
150°C - 4 minutes	○				
160°C - 4 minutes		○			
170°C - 4 minutes			○		
170°C - 8 minutes				○	
175°C - 15 minutes					○
Compound Temperature after Discharge (°C)	162	171	175	179	183
Activation Energy ① (kJ/mol)	158	158	158	158	158
Activation Energy ② (kJ/mol)	151	150	148	148	147
Change Rate (%)	4	4	6	6	6
Die Swell Ratio	1.10	1.10	1.10	1.10	1.10
Ribbon Crack Test	No	No	No	No	No
Foreign Matter ¹ (Piece/m)	0	0	0	0	0

¹ Number of foreign matter in the product

Table 3

	Comparative Example				
	1	2	3	4	5
(Mixing Conditions)					
Discharge Temp. - Mixing Time					
150°C - 4 minutes	○				
160°C - 4 minutes		○			
170°C - 4 minutes			○		
170°C - 8 minutes				○	
175°C - 15 minutes					○
Compound Temperature after Discharge (°C)	163	170	174	178	181
Activation Energy ① (kJ/mol)	158	158	158	158	158
Activation Energy ② (kJ/mol)	120	80	20	9	6
Change Rate (%)	24	49	87	94	96
Die Swell Ratio	1.08	1.03	1.02	1.00	1.00
Ribbon Crack Test	No	Crack	Break	Break	Break
Foreign Matter ¹ (Piece/m)	2	5	6	10	15

¹ Number of foreign matter in the product

Examples 6-8 and Comparative Examples 6 -8

Similar procedures to Example 1 - 5 were repeated except varying addition amount of bis-3-(triethoxysilyl)propyltetrasulfane, and mixing using a Banbury and a 8 inch ϕ roll were carried out at 170 °C for 4 min. Temperature of the compound after discharge was 175 °C.

Formulation of each composition is shown in Table 4 and mixing conditions and results are shown in Table 5.

Table 4

	Example			Comparative Example		
	6	7	8	6	7	8
(Composition) Copolymer Rubber (A-1)	110	110	110	110	110	110
Zinc Oxide No.1	5	5	5	5	5	5
Stearic Acid	1	1	1	1	1	1
Asahi #60G	175	175	175	175	175	175
Whiton SB	20	20	20	20	20	20
PW-380	85	85	85	85	55	55
Si-69	0.05	0.3	1.5	0	3	5
Sanceler 22	0.7	0.7	0.7	0.7	0.7	0.7
Sanceler BZ	1.3	1.3	1.3	1.3	1.3	1.3
Sanceler MDB	1.3	1.3	1.3	1.3	1.3	1.3
Arquad 2HT-F	1.0	1.0	1.0	1.0	1.0	1.0
Sulfur	1.0	1.0	1.0	1.0	1.0	1.0
Vesta #BS	5	5	5	5	5	5

Table 5

	Example			Comparative Example		
	6	7	8	6	7	8
(Characteristics of Unvulcanized Rubber)						
V _m (140°C)	40	40	40	40	40	40
t ₅ (125°C)	10.3	10.3	12.1	8.5	15.6	17.6
(Ribbon Crack Test)						
Presence of Crack	No	No	No	Break	No	No
Die Swell Ratio	1.10	1.10	1.10	1.02	1.10	1.10
Activation Energy ①	158	158	158	158	158	158
Activation Energy ②	143	147	150	20	151	152
Change Rate (%)	9	7	5	87	4	4
(Physical Properties of Vulcanized Rubber ¹)						
M ₁₀₀ (MPa)	3.74	3.45	3.27	4.3	3.01	2.97
M ₃₀₀ (MPa)	9.79	8.85	8.22	8.57	7.86	7.76
T _B (MPa)	11.3	11.0	10.2	9.21	11.2	11.8
E _B (%)	420	480	470	380	500	530
H _A	77	78	77	75	76	75
(Compression Set)						
70°C x 22h (%)	15	15	15	30	50	58
Foreign Matter ²						
(Piece/m)	0	0	0	6	0	0

¹ Conditions: 170°C x 10 min., 15 min. for CS

² Number of foreign matter in the product

Comparative Examples 9 -14

Similar procedures to Example 3 were repeated except for using equivalent mole of ingredient A shown in Table 6 or 0.03 or 0.3 weight parts of sulfur instead of bis-3-(triethoxysilyl)

propyltetrasulfane (mixing conditions: 170 °C for 4 min.).

Results are shown in Table 6.

Table 6

	Comparative Example					
	9	10	11	12	13	14
(Component A)						
Organosilane 1	○					
Organosilane 2		○				
Vinylsilane			○			
Accelerator TRA				○		
Sulfur (0.03 wt. parts)					○	
Sulfur (0.3 wt. parts)						○
Characteristics of Unvulcanized Rubber						
V _m (140°C)	43	42	41	43	42	68
Die Swell Ratio	1.05	1.05	1.05	1.00	1.05	NM ²
Activation Energy ①	158	158	158	158	158	NM ²
Activation Energy ②	13	15	12	10	6	NM ²
Change Rate (%)	92	90	92	94	96	
(Ribbon Crack Test)						
Presence of Crack	Break	Break	Break	Break	Break	Break
Foreign Matter ¹						
(Piece/m)	4	4	4	3	2	NM ²

¹ Number of foreign matter in the product

² Not measurable

Ingredient A:

Organosilane 1: Dimethoxymethylphenylsilane (SiC₉H₁₄O₂)

(Shin-Etsu Chem. Co., Ltd.)

Organosilane 2: Tetrakis(2-methoxyethoxy)silane

$((\text{CH}_3\text{OCH}_2\text{CH}_2\text{O})_4\text{Si})$ (Shin-Etsu Chem. Co., Ltd.)

Vinylsilane: Vinyltris(β -methoxyethoxy)silane

$((\text{CH}_3\text{OCH}_2\text{CH}_2\text{O})_3\text{SiCH}=\text{CH}_2)$ (Shin-Etsu Chem. Co., Ltd.)

Vulcanization accelerator TRA: Dipentamethylenethiuram tetrasulfide (Sanshin Chem. Ind. Co., Ltd., trade name: Sanceler TRA)

Examples 9 - 11 and Comparative Examples 15 -16 Weatherstrip sponge products

A composition consisting of the following components was mixed by 16 L Bumbury's mixer (made by Kobe Steel, Ltd.) under charge ratio of 75 % for 6 min: 100 weight parts (120 weight parts as product weight) of ethylene / propylene / 5-vinyl-2-norbornene copolymer rubber (A-2) [molar ratio of ethylene / propylene = 68 / 32, intrinsic viscosity $[\eta]$ in decalin at 135 °C = 2.7 dl/g, iodine value = 25, Mooney viscosity (ML(1+4) at 125 °C) = 45, oil content = 20 phr (parts per hundred rubber); product of Mitsui Chem. Corp.] , 5 weight parts of activated zinc white [Inoue Sekkai Kogyo K.K., trade name: MetaZ102] , 90 weight parts of SRF-H carbon black [Asahi Carbon Co., Ltd., trade name: Asahi #50HG] , predetermined amount of bis-3-(triethoxysilyl) propyltetrasulfane [Degussa Huels AG., trade name: Si-69] , 70 weight parts of paraffinic process oil [Idemitsu Kosan Co., Ltd., trade name: Diana Process Oil PW-380] and predetermined amount of activator [polyethylene glycol, NOF Corp. trade name: PEG#4000]. Temperature of discharged compound was 165 °C. Simultaneous mixing method for whole components was adopted. Predetermined amount of bis-3-(triethoxysilyl)propyltetrasulfane was sprayed on weighed carbon black and charged into the mixer simultaneously with carbon

black.

The compound thus prepared was then wound around an open roll of 8 inch ϕ (surface temperatures of front and back rolls; 50 °C, rotation speeds of front and back rolls; 18 rpm and 15 rpm, respectively) and then sulfur, vulcanization accelerator, defoaming agent (calcium oxide; Inoue Sekkai Kogyo K.K., trade name: Vesta 20) and foaming agent [p,p'-Oxybis (benzenesulfonylhydrazide), Eiwa Chem. Ind. Co., Ltd., trade name: Neocelbon N1000SW] were added and mixed for 5 min. A ribbon-like compound with 10 mm thickness and 70 mm width was sheeted out.

Vulcanization and foaming were performed using molding line with a microwave vulcanization chamber (UHF) and a hot air vulcanization chamber (HAV) connected in series or without the former. Temperatures at extruder head and UHF were set at 80 °C and 200 °C, respectively, and power was adjusted so that temperature of extrudate surface at the exit of UHF was kept at 180 °C. HAV of 30 m length was used and temperature inside the HAV was set at 250 °C.

Formulation of each composition and results are shown in Table 7.

Examples 12 Weatherstrip sponge products

A composition consisting of the following components was premixed using 4.3 L Bumbury's mixer at 175 °C for 5 min: 100 weight parts (120 weight parts as product weight) of ethylene / propylene / 5-vinyl-2-norbornene copolymer rubber (A-2) [molar ratio of ethylene / propylene = 68 / 32, intrinsic viscosity $[\eta]$ in decalin at 135 °C = 2.7 dl/g, iodine value = 25, Mooney viscosity (ML(1+4)

at 125 °C) = 45, oil content = 20 phr (parts per hundred rubber); product of Mitsui Chem. Corp.] and 20 weight parts of propylene homopolymer (melting temperature: 160 °C, MFR (190 °C, 2.16 kg load in accordance with ASTM D1238): 20 g/10 min and crystallinity: 85 %) . The compound thus mixed was extruded using 50 mm extruder at 260 °C (in nitrogen sealing), followed by cooling in water to get EPDM / PP alloy. Procedures similar to Examples 9-11 were repeated using the EPDM/PP alloy described above and formulations shown in Table 7. Results are shown in Table 7.

Table 7

	Example				Comparative Example	
	9	10	11	12	15	16
Copolymer Rubber (A-2) Polymer (A-3) (EPDM/PP)	120	120	120	140	120	120
Activated Zinc Oxide	5	5	5	5	5	5
Asahi 50HG	90	90	90	70	90	90
Si-69	0.01	0.3	1.0	0.3	3.0	0
PW-380	70	70	70	70	70	70
PEG #4000	1	1	1	1	1	4
Vesta 20	4	4	4	4	4	4
N1000SW	4	4	4	4	4	4
Physical Properties of Sponge						
M ₂₅ (KPa)	290	290	290	292	280	270
Specific Gravity	0.50	0.50	0.50	0.47	0.60	0.65
Water Absorption (wt%)	4	5	5	1	30	20
Activation Energy ①	70	70	70	70	70	70
Activation Energy ②	70	69	68	69	70	6
Change Rate (%)	0	1	1	1	0	91
Die Swell Ratio	1.30	1.30	1.30	1.29	1.30	1.00
Shape Retention (%)	91	91	91	91	90	94
Compression Set (%)	21	22	19	17	48	50
Surface Texture of Product	5	5	5	5	5	2

Vulcanization system: Sulfur 1.5 weight part, vulcanization accelerator 2-mercapto benzothiazole [Sanshin Chem. Ind. Co., Ltd. trade name: Sanceler M] 1.0 weight part, vulcanization accelerator N-cyclohexyl-2-benzothiazolesulfenamide [Sanshin Chem. Ind. Co., Ltd., trade name: Sanceler CM] 1.0 weight part,

vulcanization accelerator diethylthiourea [Sanshin Chem. Ind. Co., Ltd., trade name: Sanceler EUR] 1.0 weight part and vulcanization accelerator tetrakis(2-ethylhexyl)thiuram disulfide [Sanshin Chem. Ind. Co., Ltd., trade name: Sanceler TOT] 1.0 weight part.

Examples 13 - 17 and Comparative Examples 17 -21 Composition for rubber vibration isolators and products thereof

A composition including the following components was mixed by 16 L Bumbury's mixer (made by Kobe Steel, Ltd.) under charge ratio of 75 %: 100 weight parts (150 weight parts as product weight) of ethylene / propylene / 5-vinyl-2-norbornene copolymer rubber (A-4) [molar ratio of ethylene / propylene = 68 / 32, intrinsic viscosity $[\eta]$ in decalin at 135 °C = 4.0 dl/g, iodine value = 22, Mooney viscosity (after oil extension) = 110, oil content = 50 phr (parts per hundred rubber); product of Mitsui Chem. Corp.] , 60 weight parts of FEF carbon black [Asahi Carbon Co., Ltd., trade name: Asahi #60G] , 5 weight parts of zinc white [Sakai Chem. Ind. Co., Ltd., trade name: No. 1] and 1 weight part of stearic acid.

Mixing procedures were as follows: Ethylene / propylene / 5-vinyl-2-norbornene copolymer rubber (A-4) was masticated for 15 sec, followed by addition of zinc white, stearic acid and softening agent, and finally 0.5 weight parts (1.0×10^{-3} mole) of bis-3-(triethoxysilyl)propyltetrasulfane [Degussa Huels AG., trade name: Si-69] roughly mixed with carbon black (in Comparative Examples 17-21, carbon black was charged alone without bis-3-(triethoxysilyl)propyltetrasulfane), and mixed for 4 min. Temperature of discharged compounds was 175 °C.

The compound thus prepared was then wound around an open roll

of 8 inch ϕ (surface temperatures of front and back rolls; 50 °C, rotation speeds of front and back roll; 18 rpm and 15 rpm, respectively, roll clearance: 5 mm), and then added with sulfur and vulcanization accelerator and mixed for 5 min. A ribbon-like compound with 5 mm thickness and 40 mm width was sheeted out and fed to a vertical type injection machine to produce rubber vibration isolators.

Samples for measurement of activation energy were prepared similarly by the process described above except for excluding vulcanization agent and vulcanization accelerators in roll mixing.

Formulation of each composition is shown in Table 8 and mixing conditions and results are shown in Tables 9 and 10.

Table 8

	Example	Comparative Example
	13-17	17-21
(Composition)		
Copolymer Rubber (A-4)	150	150
Zinc Oxide No.1	5	5
Stearic Acid	1	1
Asahi #60G	60	60
Si-69	0.5	0
Sanceler BZ	1.3	1.3
Sanceler M	0.7	0.7
Sulfur	0.75	0.75

Vulcanization system: Sulfur 0.75 weight part, vulcanization accelerator zinc di-n-butyldithiocarbamate [Sanshin Chem. Ind. Co., Ltd., trade name: Sanceler BZ] 1.3 weight part, vulcanization

accelerator 2-mercaptobenzothiazole [Sanshin Chem. Ind. Co., Ltd.,
trade name: Sanceler M] 0.7 weight part.

Table 9

	Example				
	13	14	15	16	17
(Mixing Conditions)					
Discharge Temp. - Mixing Time					
150°C - 4 minutes	○				
160°C - 4 minutes		○			
170°C - 4 minutes			○		
170°C - 8 minutes				○	
175°C - 15 minutes					○
Activation Energy ① (kJ/mol)	80	80	80	80	80
Activation Energy ② (kJ/mol)	80	79	78	78	77
Change Rate (%)	0	1	3	3	4
Ribbon Break Test	No	No	No	No	No

Table 10

	Comparative Example				
	17	18	19	20	21
(Mixing Conditions)					
Discharge Temp. - Mixing Time					
150°C - 4 minutes	○				
160°C - 4 minutes		○			
170°C - 4 minutes			○		
170°C - 8 minutes				○	
175°C - 15 minutes					○
Activation Energy ① (kJ/mol)	80	80	80	80	80
Activation Energy ② (kJ/mol)	38	30	18	10	7
Change Rate (%)	53	63	78	88	91
Ribbon Break Test	Many Cracks	Break	Break	Break	Break

Examples 18-20 and Comparative Examples 22-24

A composition including the following components was mixed using 16 L Bumbury's mixer (made by Kobe Steel Ltd.) under charge ratio of 75 %: 100 weight parts (as product weight, 150 weight parts) of ethylene / propylene / 5-vinyl-2-norbornene copolymer rubber (A-4) [molar ratio of ethylene / propylene = 68 / 32, intrinsic viscosity $[\eta]$ in decalin at 135 °C = 4.0 dl/g, iodine value = 22, Mooney viscosity (after oil extension) = 110, oil content = 50 phr (parts per hundred rubber); product of Mitsui Chem. Corp.] or 100 weight parts (110 weight parts as product weight) of ethylene / propylene / 5-vinyl-2-norbornene copolymer rubber (A-5) [molar ratio of ethylene / propylene molar ratio = 68 / 32, intrinsic viscosity $[\eta]$ in decalin at 135 °C = 2.7

dl/g, iodine value = 20, Mooney viscosity (after oil extension, ML(1+4) 100 °C) = 90, oil content = 10 phr (parts per hundred rubber); product of Mitsui Chem. Corp.] , 60 weight parts of FEF carbon black [Asahi Carbon Co., Ltd. trade name: Asahi #60G] , 40 weight parts of softening agent [Idemitsu Kosan Co., Ltd., trade name: Diana Process Oil PW-380] (only in Example 20), 5 weight parts of zinc white [Sakai Chem. Ind. Co., Ltd., trade name: No. 1] and 1 weight part of stearic acid .

Mixing procedures were as follows: Ethylene / propylene / 5-vinyl-2-norbornene copolymer rubber (A-4) or ethylene / propylene / 5-vinyl-2-norbornene copolymer rubber (A-5) was masticated for 15 sec, followed by addition of zinc white, stearic acid, and softening agent (only in Example 20), and finally carbon black roughly mixed with predetermined amount of bis-3-(triethoxysilyl)propyltetrasulfane [Degussa Huels AG., trade name: Si-69] (in Comparative Examples 23 and 24, dipentamethylenethiuram tetrasulfide (Sanshin Chem. Ind. Co., Ltd., trade name: Sanceler TRA) and 0.04 weight part of sulfur were roughly blended respectively, instead of bis-3-(triethoxysilyl)propyltetrasulfane) and mixed for 4 min. Temperature of discharged compounds was 170 °C.

The compound thus prepared was then wound around an open roll of 8 inch ϕ (surface temperatures of front and back rolls; 50 °C, rotation speeds of front and back roll; 18 rpm and 15 rpm, respectively, roll clearance; 5 mm) and then added with sulfur and vulcanization accelerator and mixed for 5 min. A ribbon-like compound with 5 mm thickness and 40 mm width was sheeted out and fed to a vertical type injection machine to produce rubber vibration isolators.

Samples for measurement of activation energy were prepared similarly by the process described above except for excluding vulcanization agent and vulcanization accelerators in roll mixing.

Formulation of each composition is shown in Table 11 and mixing conditions and results are shown in Table 12.

Table 11

	Example			Comparative Example		
	18	19	20	22	23	24
(Composition)						
Copolymer Rubber (A-4)	150	150		150	150	150
Copolymer Rubber (A-5)			110			
Zinc Oxide No.1	5	5	5	5	5	5
Stearic Acid	1	1	1	1	1	1
Asahi #60G	60	60	60	60	60	60
PW-380			40			
Sanceler TRA					0.5	
Sulfur						0.04
Si-69	0.3	0.5	1.0	3.0	0	0
Sanceler M	0.7	0.7	0.7	0.7	0.7	0.7
Sanceler BZ	1.0	1.0	1.0	1.0	1.0	1.0
Sanceler TT	0.8	0.8	0.8	0.8	0.8	0.8
Sulfur	0.75	0.75	0.75	0.75	0.75	0.75

Vulcanization accelerator

Zinc di-n-butyldithiocarbamate [product of Sanshin Chem. Ind. Co., Ltd., trade name: Sanceler BZ]

2-Mercaptobenzothiazole [product of Sanshin Chem. Ind. Co., Ltd.,

trade name: Sanceler M]

Tetramethylthiuram disulfide [product of Sanshin Chem. Ind. Co., Ltd., trade name: Sanceler TT]

Table 12

	Example			Comparative Example		
	18	19	20	22	23	24
Activation Energy ①	80	80	80	80	80	80
Activation Energy ②	79	79	80	80	15	10
Change Rate (%)	1	1	0	0	81	88
(Physical Properties of Vulcanized Rubber ¹)						
M ₁₀₀ (MPa)	3.2	3.1	3.0	2.9	4.2	4.3
M ₃₀₀ (MPa)	11.8	11.2	10.8	10.1	11.8	11.7
T _B (MPa)	21.5	21.9	22.5	22.5	12.5	12.8
E _B (%)	760	770	780	790	420	410
HA	60	60	60	59	61	61
(Compression Set)						
120°C x 22h (%)	41	42	43	62	60	61
Dynamic Modulus (1Hz)						
E* (x10 ⁷) Pa	7.2	6.8	6.7	6.5	7.8	7.9
tan δ (x10 ⁻¹)	0.12	0.10	0.10	0.10	0.13	0.13
(10Hz)						
E* (x10 ⁷) Pa	8.5	8.3	8.2	8.0	9.5	9.7
tan δ (x10 ⁻¹)	0.14	0.13	0.13	0.13	0.17	0.17

¹ Conditions: 170°C x 10 min., 12 min. for CS

Example 21 and Comparative Examples 25-27 Weatherstrip sponge product.

A composition including the following components was mixed by

16 L Bumbury's mixer (made by Kobe Steel Ltd.) under charge ratio of 75 % for 6 min: 100 weight parts of ethylene / propylene / 5-vinyl-2-norbornene copolymer rubber (A-6) [molar ratio of ethylene / propylene = 68 / 32, intrinsic viscosity $[\eta]$ in decalin at 135 °C = 2.1 dl/g, iodine value = 25, Mooney viscosity (ML(1+4) 125 °C) = 30; product of Mitsui Chem. Corp.] , 5 weight parts of activated zinc white [Inoue Sekkai Kogyo K.K., trade name: MetaZ102] , 2 weight part of stearic acid , 100 weight parts of SRF-H carbon black [Asahi Carbon Co., Ltd., trade name: Asahi #50HG] , predetermined amount of bis-3-(triethoxysilyl)propyltetrasulfane [Degussa Huels AG., trade name: Si-69] or other organosilane and 40 weight parts of paraffinic process oil [Idemitsu Kosan Co., Ltd., trade name: Diana Process Oil PW-380] . Simultaneous mixing method for whole components was adopted. Predetermined amount of bis-3-(triethoxysilyl)propyltetrasulfane and other organosilane were sprayed on the surface of weighed carbon black and charged into the mixer together with carbon black.

The compound thus prepared was then wound around an open roll of 8 inch ϕ (surface temperatures of front and back rolls; 50 °C, rotation speeds of front and back roll; 18 rpm and 15 rpm, respectively), and then added with sulfur, vulcanization accelerator, defoaming agent (calcium oxide; Inoue Sekkai Kogyo K.K., trade name: Vesta 20), foaming agent [azodicarbonamide, Eiwa Chem. Ind. Co., Ltd., trade name: Vinyhole AC#3] and co-foaming agent [urea based type; Eiwa Chem. Ind. Co., Ltd., trade name: Cellpaste 101] and mixed for 5 min. A ribbon-like compound with 10 mm thickness and 70 mm width was sheeted out.

The ribbon-like compound described above was then charged to

a tubular mold of a transfer molding machine in 10 sec, followed by vulcanization and foaming at 180 °C for 3.5 min. to get a foamed molded body (sponge rubber) shown in Fig. 4. Various tests for physical properties were carried out on the vulcanized and foamed rubber molded body.

Formulation of each composition, mixing conditions and results are shown in Tables 13.

Example 22 Weatherstrip sponge product

A composition consisting of the following components was premixed in advance using 4.3 L Bumbury's mixer at 175 °C for 5 min: 100 weight parts of ethylene / propylene / 5-vinyl-2-norbornene copolymer rubber (A-6) [molar ratio of ethylene / propylene = 68 / 32, intrinsic viscosity $[\eta]$ in decalin at 135 °C = 2.1 dl/g, iodine value = 25, Mooney viscosity (ML(1+4) at 125 °C) = 30; product of Mitsui Chem. Corp.] and 20 weight parts of propylene homopolymer (melting temperature: 160 °C, MFR (190 °C, 2.16 kg load in accordance with ASTM D1238): 20 g/10 min and crystallinity: 85 %) . Thus mixed compound was extruded using 50 mm extruder at 260 °C (in nitrogen sealing), followed by cooling in water to get EPDM / PP alloy. Similar procedures to Example 21 were repeated using the alloy and ingredients shown in Table 13. Results are shown in Table 13.

Table 13

	Example		Comparative Example		
	21	22	25	26	27
Copolymer Rubber (A-6)	100		100	100	100
EPDM/PP Alloy		120			
Activated Zinc Oxide	5	5	5	5	5
Stearic Acid	2	2	2	2	2
Asahi 50HG	100	80	100	100	100
PW-380	40	40	40	40	40
Si-69	0.5	0.01			
Organosilane 1			0.3		
Organosilane 2				0.3	
Organosilane 3					0.3
Foaming Agent	7	7	7	7	7
Urea-based Co-foaming agent	2	2	2	2	2
Activation Energy ①	95	95	95	95	95
Activation Energy ②	94	94	43	34	23
Change Rate (%)	1	1	55	64	76
Temperature after Mixing and Discharge (°C)	120	123	135	135	135
Physical Properties of Sponge					
Specific Gravity (kg/cm ³)	540	550	560	565	570
T _B (MPa)	2.5	2.3	2.6	2.5	2.4
E _B (%)	290	280	200	210	190
Compression Set (%)	30	32	43	45	47
Fluidity (mm)	170	145	110	100	90
Surface Texture of Product	5	5	2	2	2

Vulcanization system: Sulfur 1.0 weight part, vulcanization

accelerator 2-mercaptobenzothiazole [Sanshin Chem. Ind. Co., Ltd., trade name: Sanceler M] 0.5 weight part, vulcanization accelerator tetramethylthiuram disulfide [Sanshin Chem. Ind. Co., Ltd., trade name: Sanceler TT] 0.5 weight part, vulcanization accelerator zinc di-n-butylthiocarbamate [Sanshin Chem. Ind. Co., Ltd., trade name: Sanceler BZ] 1.5 weight part and tetraethylthiuram disulfide [Sanshin Chem. Ind. Co., Ltd., trade name: Sanceler TET] 0.5 weight part.

Organosilane 1: Dimethoxymethylphenylsilane ($\text{SiC}_9\text{H}_{14}\text{O}_2$) (Shin-Etsu Chem. Co., Ltd.)

Organosilane 2: Tetrakis(2-methoxyethoxy)silane
 $((\text{CH}_3\text{OCH}_2\text{CH}_2\text{O})_4\text{Si})$ (Shin-Etsu Chem. Co., Ltd.)

Organosilane 3: Vinyltris(β -methoxyethoxy)silane
 $((\text{CH}_3\text{OCH}_2\text{CH}_2\text{O})_3\text{SiCH}=\text{CH}_2)$ (Shin-Etsu Chem. Co., Ltd.)

All the publications, patents and patent applications cited herein are incorporated herein by reference in their entirety.

Industrial Applicability

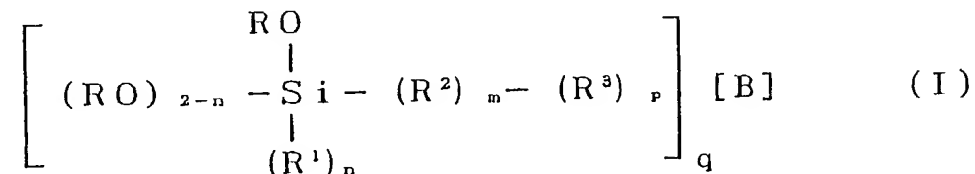
The invention provides a rubber composition for extrusion giving an extrudate having no crack nor breakage and stable cross sectional shape in ribbon-like compound prepared prior to extrusion, along with foam products having little foaming variation. This contributes to provide extrudate products such as weatherstrip sponge, high extension foam seal, glassrun channel, window frame and water hose for automobile, which have superior surface texture and stable quality irrespective to season or type of mixing machine. The invention eliminates most of inferior products which have been recognized to be caused by unknown foreign

matter until now.

A rubber composition for molding of the invention provides a compound prepared for injection which has superior fluidity in a mold and no breakage phenomenon, along with stable and uniform foaming characteristics in molded sponge. Furthermore, a rubber composition for molding of the invention provides rubber vibration isolator, cast sponge, grommet, O-ring, packing, boots, window frame, break piston cup and OA roll products with good surface texture and superior mechanical strength.

CLAIMS

1. A rubber composition for extrusion comprising 100 weight parts of ethylene / α -olefin / non-conjugated polyene copolymer rubber (A) composed of ethylene, α -olefin having carbon atoms of 3 - 20 and non-conjugated polyene, and at least 30 - 300 weight parts of carbon black (B) and 1.0×10^{-5} - 5.0×10^{-3} mol of alkoxy silane compound (C) shown by the following formula (I):



wherein, R is an alkyl group having carbon atoms of 1 - 4 or an alkoxy group having carbon atoms of 1 - 4, R^1 is an alkyl group having carbon atoms of 1 - 4 or phenyl group, n is 0, 1 or 2, R^2 is a bivalence of linear or branched hydrocarbon group having carbon atoms of 1 - 6, R^3 is an arylene group having carbon atoms of 6 - 12, m and p are 0 or 1 respectively, and m and p are not 0 at a same time, q is 1 or 2, B is -SCN or -SH when q is 1, and -Sx- when q is 2 (wherein x is an integer of 2 - 8).

2. The rubber composition for extrusion according to claim 1, wherein the ethylene / α -olefin / non-conjugated polyene copolymer rubber (A) (i) comprises a unit (a) derived from ethylene and a unit (b) derived from α -olefin having carbon atoms of 3 - 20 in a [(a) / (b)] molar ratio of 50 / 50 - 90 / 10, (ii) has an iodine value of 1 - 40, and (iii) has an intrinsic viscosity

[η] measured in decalin at 135 °C of 2.0 - 4.5 dl/g.

3. The rubber composition for extrusion according to claim 1, wherein an amount of the carbon black (B) is 50 - 200 weight parts to 100 weight parts of the ethylene / α -olefin / non-conjugated polyene copolymer rubber (A).

4. The rubber composition for extrusion according to claim 1, wherein an amount of the carbon black (B) is 61 - 200 weight parts to 100 weight parts of the ethylene / α -olefin / non-conjugated polyene copolymer rubber (A).

5. The rubber composition for extrusion according to claim 1, wherein an amount of the carbon black (B) is 70 - 200 weight parts to 100 weight parts of the ethylene / α -olefin / non-conjugated polyene copolymer rubber (A).

6. The rubber composition for extrusion according to any one of Claims 1 - 5, wherein its apparent activation energy is 20 - 300 kJ/mol, and a change rate of the apparent activation energy is not higher than 40% even after processing in any rubber processing process.

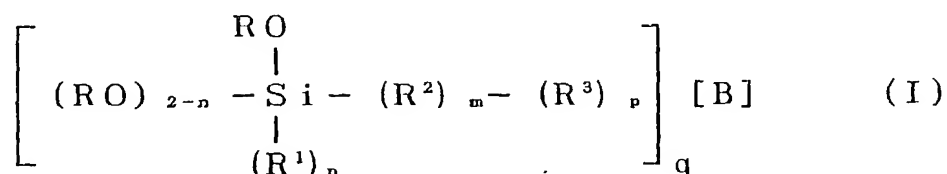
7. A rubber composition for extrusion, wherein it does not show any ribbon break nor ribbon crack, and has a change rate in die swell ratio not higher than 5% due to a rise of viscosity in an extruder.

8. A weather strip sponge product, highly expanded seal product, glass run channel product, window frame product or water hose product for automobile characterized by comprising the rubber composition according to any one of claims 1 - 7.

9. A process for manufacturing a vulcanized rubber molding product comprising molding the rubber composition according to any one of claims 1 - 7 to an intended shape using an extruder and

vulcanizing it.

10. A rubber composition for molding comprising 100 weight parts of an ethylene / α -olefin / non-conjugated polyene copolymer rubber (A) composed of ethylene, α -olefin having carbon atoms of 3 - 20 and non-conjugated polyene, and at least 30 - 300 weight parts of carbon black (B) and 1.0×10^{-5} - 5.0×10^{-3} mol of alkoxy silane compound (C) shown by the following formula (I):



wherein, R is an alkyl group having carbon atoms of 1 - 4 or an alkoxy group having carbon atoms of 1 - 4, R^1 is an alkyl group having carbon atoms of 1 - 4 or phenyl group, n is 0, 1 or 2, R^2 is a bivalence of linear or branched hydrocarbon group having carbon atoms of 1 - 6, R^3 is an arylene group having carbon atoms of 6 - 12, m and p are 0 or 1 respectively, and m and p are not 0 at a same time, q is 1 or 2, B is -SCN or -SH when q is 1, and -Sx- when q is 2 (wherein x is an integer of 2 - 8).

11. The rubber composition for molding according to claim 10, wherein the ethylene / α -olefin / non-conjugated polyene copolymer rubber (A) (i) comprises a unit (a) derived from ethylene and a unit (b) derived from α -olefin having carbon atoms of 3 - 20 in a [(a) / (b)] molar ratio of 50 / 50 - 90 / 10, (ii) has an iodine value of 1-40, and (iii) has an intrinsic viscosity $[\eta]$ measured in decalin at 135 °C of 0.8 - 4.5 dl/g.

12. The rubber composition for molding according to claim 10,

wherein an amount of the carbon black (B) is 50 - 200 weight parts to 100 weight parts of the ethylene / α -olefin / non-conjugated polyene copolymer rubber (A).

13. The rubber composition for molding according to claim 10, wherein an amount of the carbon black (B) is 61 - 200 weight parts to 100 weight parts of the ethylene / α -olefin / non-conjugated polyene copolymer rubber (A).

14. The rubber composition for molding according to claim 10, wherein an amount of the carbon black (B) is 80 - 200 weight parts to 100 weight parts of the ethylene / α -olefin / non-conjugated polyene copolymer rubber (A).

15. The rubber composition for molding according to any one of Claims 10 - 14, wherein its apparent activation energy is 20 - 200 kJ/mol, and a change rate of the apparent activation energy is not higher than 20% even after processing in any rubber processing process.

16. The rubber composition for molding according to any one of claims 10 - 15, wherein, the composition does not break in a ribbon preformed prior to injection and has a good fluidity in mold which does not vary, and physical properties of the composition after vulcanization do not vary depending on mixing conditions in a preparation of the compound.

17. A rubber vibration insulator, cast sponge, grommet, O-ring, packing, boots, window frame, break piston cup or OA roll product characterized by comprising the rubber composition according to any one of claims 10 - 16.

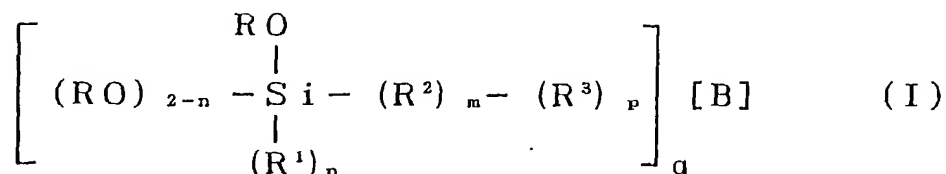
18. A process for manufacturing a vulcanized rubber molding product

comprising forming the rubber composition according to any one

of claims 10 - 16 to a shape suitable to a molding machine and
then vulcanizing it.

ABSTRACT

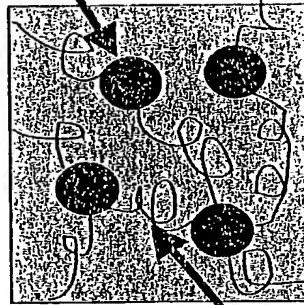
This invention relates to a rubber composition for extrusion and molding comprising 100 weight parts of ethylene / α -olefin / non-conjugated polyene copolymer (A) composed of ethylene, α -olefin having carbon atoms of 3-20 and non-conjugated polyene, and at least 30-300 weight parts of carbon black (B), and $1.0 \times 10^{-5} - 5.0 \times 10^{-3}$ mol of an alkoxy silane compound shown by the following formula (I):



wherein, R is alkyl or alkoxy, R^1 is alkyl or phenyl, n is 0, 1 or 2, R^2 is a bivalent hydrocarbon, R^3 is arylene group, m and p are 0 or 1 respectively, and m and p are not 0 at a same time, q is 1 or 2, and B is -SCN or -SH when q is 1, and -S_x- when q is 2 (wherein x is an integer of 2 - 8).

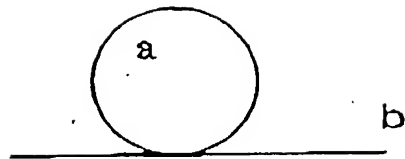
F I G . 1

Carbon Black



Network (Physical Bond)

F I G . 2



F I G . 3

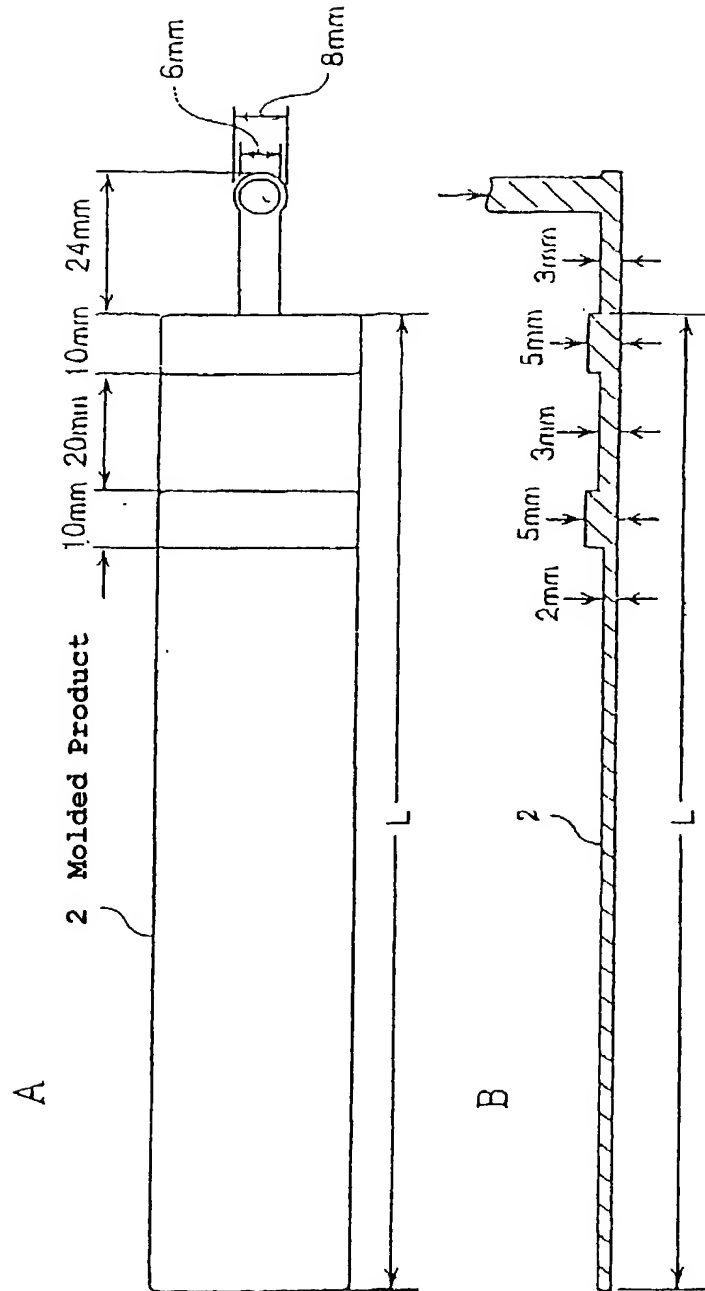
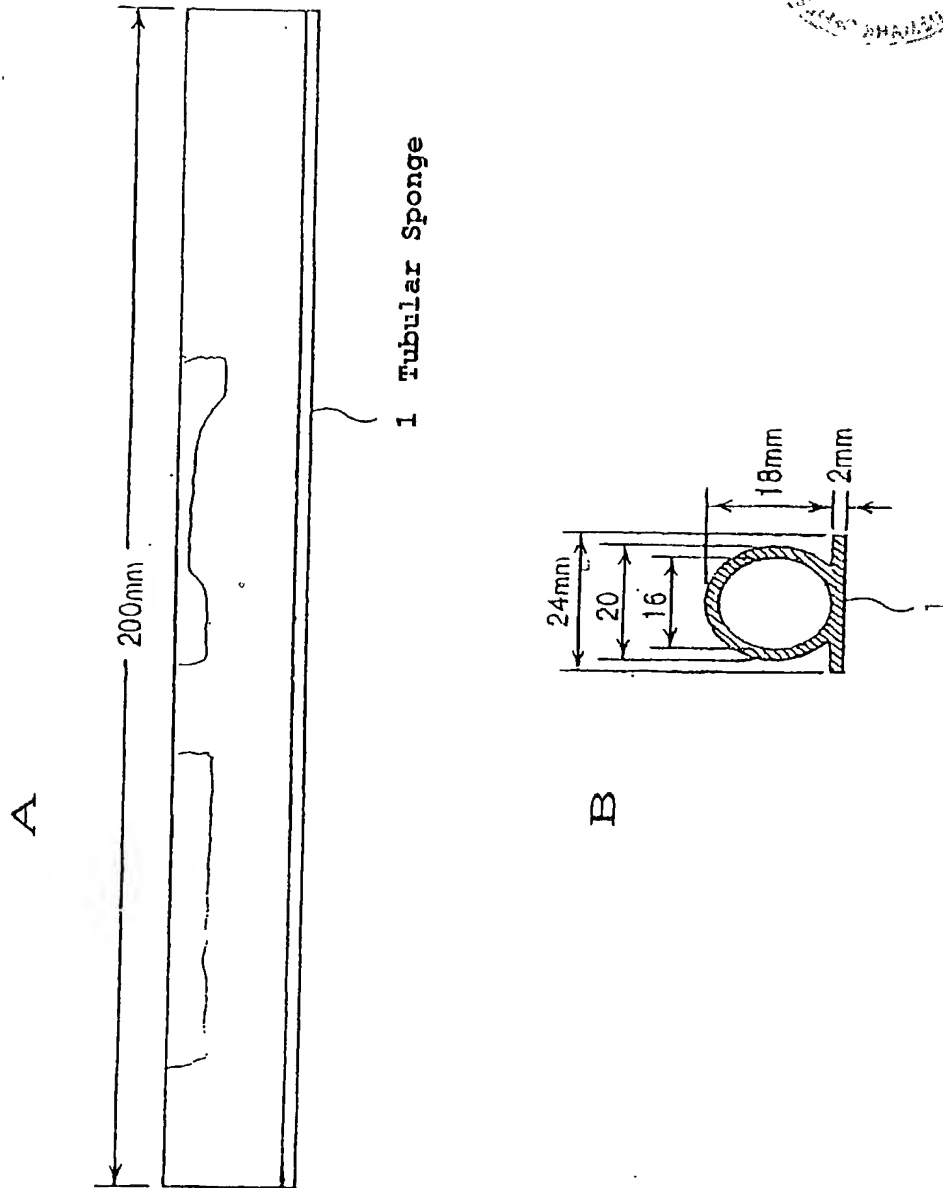


FIG. 4



1254-0193P

Attorney's Docket No.: _____

DECLARATION, POWER OF ATTORNEY AND PETITION

I (We), the undersigned inventor(s), hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I (We) believe that I am (we are) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled

A RUBBER COMPOSITION FOR EXTRUSION AND MOLDING AND APPLICATIONS
THEREOF

the specification of which

☐ is attached hereto.

☒ was filed on January 23, 2002 as

Application Serial No. 10/031,635

and amended on _____.

☒ was filed as PCT international application

Number PCT/JP00/04893

on July 21, 2000,

and was amended under PCT Article 19

on _____ (if applicable).

I (We) hereby state that I (We) have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above; that I (We) do not know and do not believe that this invention was ever known or used before my invention or discovery thereof, or patented or described in any printed publication in any country before my invention or discovery thereof, or more than one year prior to this application, or in public use or on sale in the United States for more than one year prior to this application; that this invention or discovery has not been patented or made the subject of an inventor's certificate in any country foreign to the United States on an application filed by me or my legal representatives or assigns more than twelve months before this application.

Application Serial No.	Filing Date	Status (pending, patented, abandoned)
_____	_____	_____
_____	_____	_____
_____	_____	_____

And I (We) hereby appoint: Raymond C. Stewart, Registration No. 21,066; Terrell C. Birch, Registration No. 19,382; Joseph A. Kolasch, Registration No. 22,463; Anthony L. Birch, Registration No. 26,122; James M. Slattery, Registration No. 28,380; Bernard L. Sweeney, Registration No. 24,448; Donald C. Kolasch, Registration No. 23,038; Michael K. Mutter, Registration No. 29,680; Charles Gorenstein, Registration No. 29,271; Gerald M. Murphy, Jr., Registration No. 28,977; Leonard R. Svensson, Registration No. 30,330; Terry L. Clark, Registration No. 32,644; Marc S. Weiner, Registration No. 32,181; and Andrew D. Meikle, Registration No. 32,868.

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I (We) declare further that all statements made herein of my (our) knowledge are true and that all statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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